

Groundwater Monitoring Plan  
Residential Well Water Sample Collection and Analysis at the  
Bechel Mine on the Richardson Property,  
Town of Frankfort Section 10 T24N, R 14W, Pepin County, WI

1. GENERAL

The Town of Frankfort requires collection of ground water samples for basic groundwater parameters, coliform bacteria, lead, arsenic, turbidity, nitrates, chlorides, and acrylamide for those water supply wells within ½ mile of the Bechel Mine on the Richardson Property in the Town of Frankfort, Wisconsin. It is anticipated the project will be completed in 3 phases. Phase 1 involves the collection of pre-project samples (background samples), phase 2 involves the collection of project samples (samples collected while the mine is actively removing silica sand), and phase 3 involves the collection of post project samples (after reclamation material placement is completed). The sample collection network will consist of 12 residential wells.

The project is in Section 10 of the Town of Frankfort, WI (T24N R14W). Figure 1 shows the approximate location of the residences which will be the sampling sites. At each site ground water samples will be collected and analyzed as described in this scope of work and the attached sampling protocol. Monitoring of the basic groundwater parameters of specific conductance, pH, and turbidity will be completed at each site as will sampling for specific chemical and biological parameters.

The project will begin before the extraction of silica sand at the Bechel Mine site (a limestone quarry has been in operation at this location over the past 30 years) scheduled to occur on June 1, 2012. Phase 2 of the project should be complete by 2042. Phase 3 may extend into 2050 to complete the post project data collection.

2. OBJECTIVE

The monitoring objective is to characterize pre-project groundwater conditions in the surrounding residential wells, monitor the range of impact of the mining operation, and ensure that residential well water quality meets State and Federal water quality criteria after the project is completed. Analytical methods were selected on the basis of ability to detect potential contaminants at low levels. Low level data is required to determine the effects of the project. Data collected will be used to assess the effects of this operation on the surrounding groundwater quality.

3. LOCATION OF THE WELLS

The approximate locations of the wells are shown on Figure 1. Twelve residential wells will be sampled. The proposed residential wells to be sampled are subject to landowner approval. Each landowner will be contacted prior to each sampling event so the landowner knows when and who will be on their property. Access to residential tap water sources shall be agreed upon fully with the landowners and all tenants. **All residential wells will be sampled from an exterior spigot that is not connected to a water treatment system** (i.e. water softener). The names and addresses of the residents or a contact that is able to provide access to the residential wells will be provided by the Town of Frankfort. The wells anticipated to be involved in the monitoring are presented in Table 1.

#### 4. COLLECTION OF SAMPLES

Ground water samples will be collected by a third party Sampling Consultant independent of the mining operation and the Town of Frankfort. Sampling is anticipated to begin in May 2012. Sampling is anticipated to consist of pre-project, project and post project sample rounds. The anticipated sample collection schedule is presented in Tables 1 and 2.

The Sampling Consultant will provide all suitable sample containers, equipment, and trained personnel to collect the samples. In addition, sampling equipment shall be rinsed with distilled-deionized water before each new well is sampled. Sampling will be accomplished following the attached sampling protocol. Any deviations from the protocol must be identified and approved by the Town.

Residential well samples will be collected according to the monitoring well sampling protocol with the following modifications.

- a. Unfiltered (whole water) samples will be collected and analyzed.
- b. Residential samples will be obtained from outdoor taps. Water shall be run long enough to ensure that "old or stale" water residing in the system (pipes, well, storage tank) is purged prior to sampling.
- c. Pumping volumes and times for residential wells must be recorded.
- d. Inspect taps to ensure there is no aerator attached.
- e. Samples will be obtained directly from the tap or connected flow cell for residential wells. Care will be taken to collect samples with minimal disturbance to the sample (minimal turbulence and aeration, low discharge rate).

#### 5. REQUIREMENTS – Parameters, Methods, and Detection Limits

The Sampling Consultant will analyze each sample according to Tables 2 and 3 as soon as possible after collection and within the recommended holding times for the parameters analyzed. Methods listed in Table 3 will be used. Sample analyses between the laboratories practical quantitation limit (PQL) but above the method detection limit (MDL) will be reported and qualified as "estimated". All supporting QA/QC documentation shall be included with the test results. Specific description of the analytical methods used and the detection limits attained for each parameter shall be reported with the analytical results.

The Sampling Consultant shall provide chain of custody sheets to be filled out by the sample collection teams and laboratory personnel. At a minimum, the custody sheets shall indicate project name, sample location, field observations, type of sampler used, field id number, date and time of sample, sample depth, sampling team, lab number, date received by the lab, date analyzed by the lab, and the parameters to be analyzed with their measurement units.

#### 6. QUALITY ASSURANCE/CONTROL PROTOCOL

##### General

Any laboratory performing analytical work must be state certified (Wisconsin certification or reciprocity with the Wisconsin certification program) for the parameters to be analyzed unless specifically noted (Acrylamide analysis is not Wisconsin State certified as of this writing). Normal chain of custody and other quality control procedures will be followed by the Sampling Consultant. These procedures are outlined in the sampling protocol. Standard quality control procedures will be followed and reported with the analytical results.

##### Project Specific – Sample Collection

The Sampling Consultant will provide a quality assurance/quality control protocol for sample collection. It shall describe sampling procedures and sampling equipment including pumps, bailers, and sample containers. The protocol shall also describe the procedures used to sample the private wells.

#### Project Specific – Analytical Work

The Sampling Consultant's quality assurance plan must include, as a minimum, the following elements:

- a. SAMPLE HANDLING, CUSTODY, PRESERVATION, AND HOLDING TIME.
- b. PRECISION – Replicate Samples – The Sampling Consultant will conduct replicate analyses on laboratory analyzed parameter for a minimum of 1 of the water samples analyzed per round.
- c. BLIND SAMPLES – The Sampling Consultant may collect and analyze a blind sample for each parameter using normal analytical procedures and shall report the results for evaluation in order to evaluate analytical irregularities. Blind samples will constitute less than 10% of the total sample analysis.

## **7. PRODUCTS**

The Sampling Consultant will provide a brief written report (Sampling and Analysis report) including the analytical results in tabular form, specific description of analytical methods, description of field and laboratory quality control and quality assurance measures, description of any unusual observations about the tests, and any other relevant information. The Sampling Consultant will highlight results in the report and spreadsheet that are detected above EPA/WDNR drinking water standards. The written narrative of the report will summarize the project's monitoring program (including maps and drawings of the sampling locations), review the analytical results for each sample location and discuss any data trends or results that are a probable consequence of the mining operation.

Minimum data reporting elements include:

1. field sample identification number,
2. laboratory sample number,
3. date of sample(s) collection,
4. analysis parameter(s),
5. parameter value or result,
6. concentration units,
7. all data qualifiers assigned
8. any special problems associated with an analysis,
9. final chain of custody sheets,
10. supporting QA/QC data.

## **8. COMPLETION AND DELIVERY**

The Sampling Consultant will complete the analyses and deliver the results for each sampling trip Daniel Fedderly Management Consultant for the Town of Frankfort within 45 working days after the samples are collected by the Sampling Consultant on-site. The results of in situ measurements made at the wells (pH, turbidity, specific conductance) shall be provided by mail, e-mail, or fax to Mr. Daniel Fedderly within 5 days of sample collection.

**Table 1 - Residential Well Owners and Distance from Mine Boundary**

Well Owners within ¼ mile	Well Owners ¼ to ½ mile
Randy Richardson (Well No. 4)	Donovan Eggert
Troy Gates (abandoned residence)	Diane Stewart
Larry Baker	Edward Richardson
John Ryan	Kathleen Rutherford
Tim Brusoe (Well No.3)	Todd Biles
	Donald Gisch
	Randy Richardson (Well No. 1 & 2)

Well Numbering refers to Figure 1

**Table 2 - Frankfort/Bechtel Mine Sample Parameters for 12 Residential Wells**

SCHEDULE	Phase 1 – Pre Silica Sand Mining	Phase 2 – Silica Sand Mine Operational		Phase 3 Post Reclamation
Sampling Frequency	May, July 2012	Quarterly (within ¼ mile or ½ mile if down gradient of Mine Site)	Semiannual (within ½ mile of site)	Annual (within ½ mile of site)
Basic Parameters <sup>1</sup>	X	X	X	X
Nitrates, Chlorides, Total Suspended Solids	X	X	X	X
Metals (Lead, Arsenic)	X	X	X	X
Acrylamide	X	X		X

1 – Basic parameters are water specific conductance, pH, and turbidity

**Table 3 – Water Analysis**

Parameter	Test Method+	Test Method PQL*
Nitrate Nitrogen	EPA 352.1 or 353.2	0.1 mg/l
Coliform Bacteria	Presence-absence, MF, MMO-MUG; MTF	0.1/100ml-
Chlorides	EPA 300.0 or 325.2	0.1 mg/l
Total Suspended Solids	EPA 160.2 or 2540D	1.6 mg/l
Arsenic	EPA 200.7 or 206.2	0.1 µg/L
Lead	EPA 200.7 or 239.2	1 µg/L
pH	EPA 150.1	0.1 std units
Specific Conductance	EPA 120.1	1 µs/cm
Turbidity	EPA 180.1	1 ntu
Acrylamide	EPA 8316	8 µg/l

\*Practical Quantitation Limit

+ Laboratory Method is subject to change as based on Laboratory Certification and Detection Equipment Used. Laboratory Method used will be EPA Method as described in SW-846

Detection limits refer to final analyte concentrations, including back calculations, and do not refer to the basic instrument detection limits. All detection limits are minimum acceptable levels.

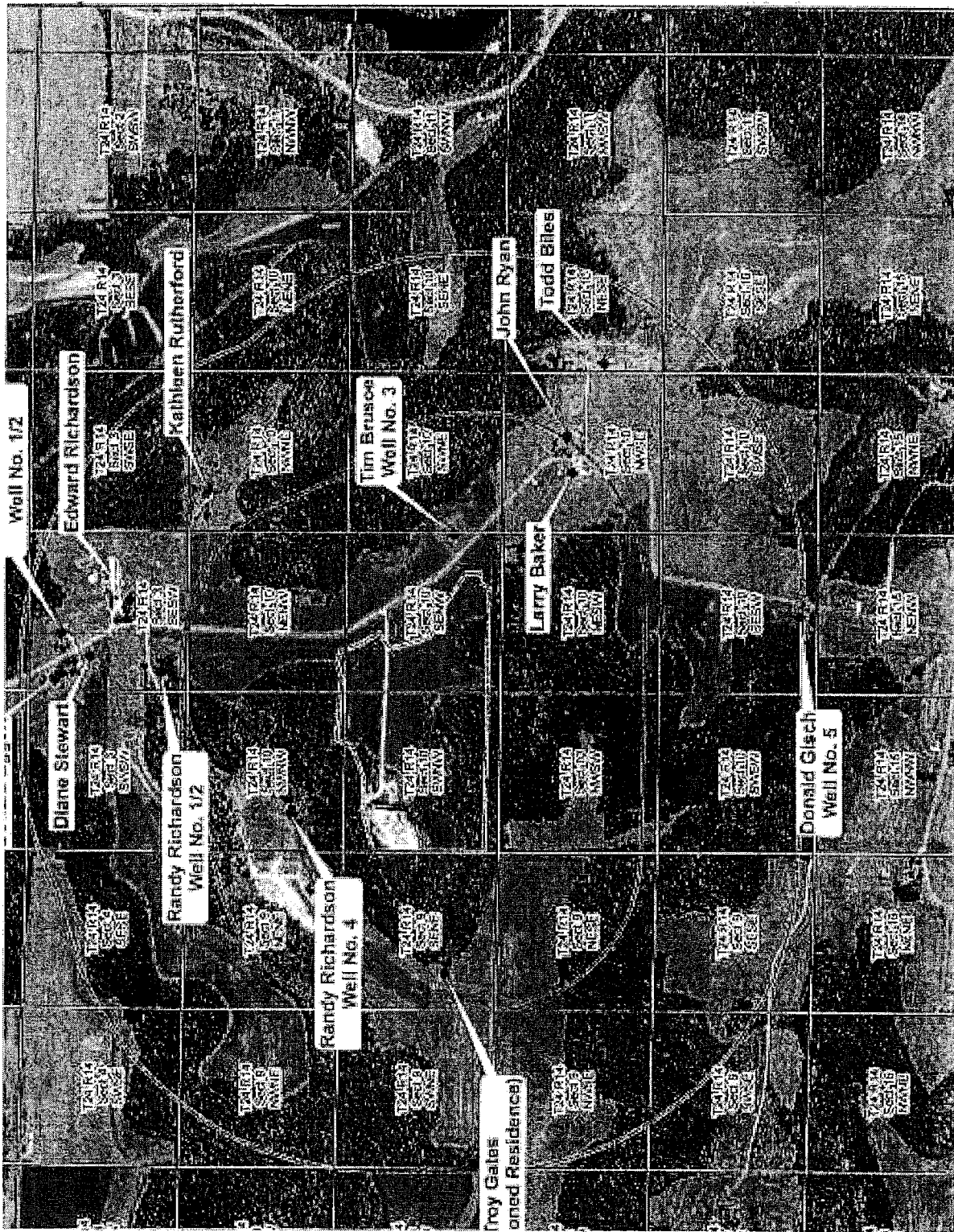


Figure 1. Map of the project location

# FRANKFORT RESIDENTIAL WELLS SAMPLING PROTOCOL

## 1.0 INTRODUCTION

This document defines procedures to be used for ground water quality measurements and for collecting and handling residential ground water samples obtained for the Bechel Mine Site. Deviations from these procedures may be required by unforeseen circumstances that develop during the program. Deviations from the established procedures will be evaluated as soon as possible after sampling and needs for re-sampling will be evaluated. Deviations from the specified procedures will be clearly noted and will be included in the Sampling and Analysis Report.

## 2.0 ADVANCE PREPARATION FOR SAMPLING

Selection of analytical parameters, field measurement and sampling techniques, equipment selection and other quality assurance measures are based on the sampling objectives presented in the Scope of Work.

### 2.1 Selection of Analytical Parameters

Analytical parameters were selected based on regulatory requirements and a review of site history. Samples will be collected and analyzed for the parameters in the Scope of Work.

### 2.2 Detection Limits

Minimum detection levels are shown in the Scope of Work. In all cases, these detection limits are at or below applicable action levels.

### 2.3 Quality Assurance for Field Procedures

Particular care will be exercised to avoid the following common ways in which cross contamination or background contamination may compromise ground water samples:

1. improper storage or transportation of equipment
2. contaminating the equipment or sample bottles on site by setting them on or near potential contamination sources such as uncovered ground, a contaminated vehicle, or vehicle exhaust
3. handling bottles or equipment with dirty hands or gloves
4. inadequate cleaning of well purging or sampling devices

Special care will be exercised to prevent cross-contamination of sampling equipment, sampling bottles, or anything else that could potentially compromise the integrity of samples. Field methods quality assurance verification procedures are described in Section 4.4, "Field Blanks, Replicates and Split Samples". Field personnel will work under the assumption that contamination exists in land surface soil and vegetation near sampling points, wash water, etc. Therefore, exposure to these media will be minimized by taking at least the following precautions:

1. minimizing the amount of rinse water left on washed materials
2. minimizing the time sampling containers are exposed to airborne dust or volatile contaminants in ambient air
3. placing equipment on clean, ground-covering materials instead of on the land surface

Clean gloves made of appropriately inert material will be worn by all field crew. Gloves will be kept clean while handling sampling-related materials. The gloves will be replaced by a new pair when soiled and between each sampling site.

#### **2.4 Sampling Containers and Preservatives**

Laboratory-supplied sampling containers and preservatives to be used for samples from all wells are shown in Table 1. The Sampling Consultant is responsible for ensuring that all sample collection containers are appropriate for the analysis and detection levels required. Chemical preservatives will be added in the laboratory before samples are collected.

#### **2.5 Decontamination and Storage of Equipment**

All sampling-related equipment including filtration devices, personal protection gear and materials coming into contact with actual sampling equipment or with sampling personnel will be decontaminated. If using sampling pumps and tubing that are permanently installed or dedicated to individual wells, they are exempt from field decontamination. Decontamination will be performed before, between and after working at each sampling point. All equipment will be handled in a manner that will minimize cross-contamination between wells and avoid introducing surface or ambient air contamination into a well. Equipment used during purging or sampling will be thoroughly cleaned prior to use in each individual well even when the wells are located close to each other. After cleaning, the equipment will be visibly inspected to detect sticky residues or other substances that may survive normal cleaning. If inspection reveals that decontamination was insufficient, additional measures will be implemented as needed and documented.

Decontamination procedures will be specific to the Sampling Consultants sampling plan. As the sampling of residential wells will be completed using an external spigot it is not anticipated that the well casing will be accessed during the sampling procedure, however, in the event that the water supply well must be opened for sampling then equipment will be decontaminated in the following manner:

- A. Equipment that does not contact sample water or the inside of the well
  1. Clean (inside and out where possible) with a hot water pressure washer filled with clean water
  2. Clean (inside and out ) with an Alconox/clean-water solution - applied with a scrub brush where practical
  3. Rinse with clean control water
  4. Inspect for remaining particles or surface film and repeat cleaning and rinse procedures if necessary
  
- B. The following steps shall be used for equipment that contacts sample water or the inside of the well:
  1. Clean (inside and out where possible) with an Alconox/clean-water solution - applied with a scrub -brush made of inert materials
  2. Rinse with clean control water
  3. Inspect for remaining particles or surface film and repeat cleaning and rinse procedures if necessary
  4. Rinse with an inorganic desorbing agent
  5. Rinse with clean control water
  6. Rinse thoroughly with laboratory controlled deionized water
  7. Shake off remaining water and allow to air dry

When transporting or storing equipment after cleaning, the equipment will be protected in a manner that minimizes the potential for contamination. Sampling pumps will be totally enclosed in a clean case capped at both ends. If the case is used to transport used pumps, the case will undergo the same decontamination

process as the pump before being used again. The tubing will be placed in a clean, inert plastic bag.

### **2.7 Selection of Sample Collection Techniques**

Sample collection techniques as detailed in this document have been tailored to the goals of this sampling event and the individual characteristics of this site. The techniques described herein are scientifically sound and widely used in this industry.

## **3.0 PRELIMINARY FIELD WORK**

The following procedures will be implemented to ensure representativeness of samples collected by methods in Section 4, "Sample Collection".

### **3.1 Field Inspections and Field Decisions**

Before purging or sampling, all wells will be inspected to verify that the seal is intact at the surface. The condition of any relevant facts regarding the general physical condition of the well, the surrounding soil and vegetation or other objects in the immediate vicinity of the well will be inspected. Any unusual condition including the presence of wind-blown dust or odor in the ambient air will be recorded in the Field Log. Details will be noted in the field sampling log and summarized in the Sampling and Analysis report. More specifically, any hint of odor or free product in the well will be noted in the Field Log and in the Sampling and Analysis Report. If any condition that may interfere with obtaining representative analytical results is discovered, the condition will be rectified before sampling of the dissolved phase of well water proceeds. The decision and exact change of procedure will be recorded in the Field Log and reported in the Sampling and Analysis Report in a manner that clearly indicates which data sets may have been affected by the change in protocol.

### **3.2 Detection Of Immiscible Layers**

Daniel Fedderly shall be notified as soon as possible if immiscible layers of contaminants (free product "floaters" or "sinkers") are suspected or seen or if odors or an oil sheen are observed in the well or sampling equipment. Any detection of an immiscible shall be documented in detail.

### **3.3 Water-Level Measurements**

Water level measurements are not required for the residential wells.

### **3.4 Field Water-Quality Measurements**

Specific conductance, pH, and turbidity will be measured in the field immediately before sample collection. Calibration information and all measurements will be recorded in the Field Log. All measurements except turbidity, unless measured in situ, will be completed such that measurement of these parameters will be completed while minimizing changes in temperature, pressure, and dissolved gases from the in situ aquifer environment.

The operation of the probes will be as follows:

1. The flow of ground water through the flow cell will be maintained as continuous and steady as practical throughout the measurement period.
2. Discharge velocities through the flow cell are kept low to prevent streaming potential problems with probes.



3. All probes will be fully immersed without touching the sides of the air tight, non-metallic flow cell.
4. All probes will be allowed to equilibrate with fresh well water for five minutes before recording measurements.

Specific procedural details for measurement of individual field water quality parameters are specified below. General care, maintenance, calibration procedures, and operation of each measurement device will also follow manufacturer's specifications as detailed in the instruction/owner's manual for each device.

### **Specific Conductance**

The conductivity meter will be calibrated each day using a traceable standard potassium chloride reference solution before taking measurements at the first site. Calibration shall be near the range of suspected readings. The expected range of specific conductance for this study is 200 to 600 us/cm. Linearity of the probe should be checked with a second standard. A post calibration will be completed following the day's sampling. Records of the pre-and post-calibrations shall be included with the daily data. The conductivity cell will be inspected to be sure it is in good condition with no chips in the coating.

The conductivity standard calibration solution will be labeled to show the date of preparation, check-marked to show the number of times used and replaced at regular intervals of no more than three months or 10 uses, whichever comes first. The probe will be fully immersed but will not be allowed to touch the non-metallic container. This reading will be compared with the chart value for the standard reference solution at the temperature of the solution. All readings must be corrected (temperature) to show the specific conductance (SC). It should be noted if the instrument electronically corrects for temperature. If the instrument does not correct for temperature the specific conductance (electrical conductance (EC) corrected to 25 degrees Celsius) will be calculated from the EC and the water temperature. The SC value will be taken from the conversion table provided in the EC meter instruction manual and recorded. The SC (not EC) will be used to determine when stabilization is reached. Both the electrical conductivity (EC) and temperature corrected specific conductance (SC) shall be recorded in micro-Mhos/cm, as well as the sample temperature in degrees Celsius. All readings shall be recorded on the appropriate field forms in micro-Mhos/cm to three significant digits.

### **pH**

Personnel using pH measuring equipment will read the manufacturer's instruction manual carefully before recording any measurements. Special care will be taken to protect the fragile glass bulb on the end of the pH electrode. Careful handling includes all steps from the manner in which the cap is taken off the electrode and includes keeping the electrode tip moist between sampling points.

Before sampling is begun for the day, the pH meter will be calibrated by a two-point calibration method. Periodic checks using a single buffer during the day are recommended. The single buffer calibration will normally be accomplished using a pH = 7 buffer for natural waters. At the completion of the days monitoring the pH meter will be post calibrated using the two-point calibration method.

For the two-point calibration method, two buffers with pH values representative of the range of values expected in the field will be used to check the slope (span) of the meter. Typically, a pair of buffers with pH = 7 and 10 will be used for the two-point calibration.

Because the pH of buffer solutions vary with temperature, the actual pH (e.g., pH = 7.07 vs. 7.00) of the buffer solution at its current temperature will be used for calibration. The actual pH of the buffer at its temperature of measurement will be determined from manufacturer documentation accompanying the buffer. The exact pH of the buffer solutions at 2- to 5-degree intervals for the range of buffer temperatures expected will be recorded in indelible ink on the buffer solution bottles. Only fresh buffer solutions will be used. Care will be taken not to dilute or contaminate the buffer solutions. Buffer solutions will be discarded after the

tenth calibration or four weeks after the first use of the solution, whichever occurs first. pH meter calibration will be performed as follows:

1. The pH meter's temperature compensation control will be set to the current temperature of the buffer solution.
2. The pH meter electrode will be rinsed with distilled water and the excess water will be shaken off.
3. The electrode will then be stirred and left immersed in the buffer container until it stabilizes.
4. While immersed in the first buffer solution, the calibration control will be adjusted until the display matches the known pH of the buffer.
5. Steps 2 and 3 will then be repeated to prepare for the second buffer. 6. Step 4 will be repeated for the second buffer.
6. If measurement of the second buffer does not give a satisfactory reading the slope control will be adjusted.
7. Steps 2-7 will be repeated until both buffer solutions yield satisfactory readings (within approximately 0.02 pH units of the actual value on both ends of the measured scale).
8. In the field, step 2 will be repeated at each well before measuring the pH of well water.

After allowing the pH probe to equilibrate with a continuously replenished supply of fresh aquifer water for a minimum of five minutes, the first pH measurement will be recorded.

### **Turbidity**

Turbidity meter calibration and measurement techniques will follow manufacturer recommendations. Measurements will be made inside a glass or transparent plastic bottle filled directly from well discharge in the same manner as samples are collected. Measurements will be taken immediately after filling the container to minimize bias due to particulate settling.

## **3.5 Well Purging And Stabilization**

### **Residential Wells**

The residential wells will be sampled at an exterior tap on the residences determined by the Town of Frankfort. The volume of water in the system will need to be estimated to ensure three well or system volumes have been pumped before stabilization readings are taken and samples obtained.

1. The well will be purged by withdrawing water by running the water supply well pump for a period of time estimated to be three times the water system volume in gallons divided by the pump rate in gallons per minute.
2. Sampling will immediately follow purging.
3. Well evacuation will be continuous between purging and sampling.
4. The well pump will be used for both purging and sampling at each individual well.
5. Neither air lift pumps nor any other method device that significantly aerates well water or otherwise creates significant turbulence will be used at any time during the purging or sampling of wells.

Field water quality parameters will be measured for stabilization after each water-column volume is purged. One water-column volume is defined here as equal to the volume of a cylinder with a height (h) equal to that of the Static Water Column inside the well and a diameter (d) equal to the diameter of the well casing ( $\text{Volume} = \Pi(d/2)^2 h$ ). The following target criteria for three consecutive measurements (one water-column volume apart)

will be used to demonstrate stabilization:

1. pH +/- 0.04 units temperature
2. +/- 0.1 degrees Celsius
3. specific conductance (temperature corrected EC) +/- 5%
4. dissolved oxygen +/-0.5 mg/L

Samples for laboratory analysis will be collected only after a minimum of three water-column volumes have been purged and stabilization of field water-quality parameters has been demonstrated by meeting the target criteria defined in the preceding paragraph. If field parameters do not stabilize after approximately five water-column volumes, then field staff will check operator procedures, equipment functioning and well construction information for potential problems. If all the checks produce no new insight, a decision might be made to collect samples after five water-column volumes have been purged even if field measurements have not stabilized. Before authorizing the laboratory to analyze samples, the meaningfulness and value of completing laboratory analysis of the sampling suite will be evaluated by reviewing the results of field measurements, well construction data, site hydrogeology, etc. Where such data is presented, it will be clearly documented that stabilization was not achieved; at a minimum, this fact will be reported in the Field Log and in the Sampling and Analysis Report.

## **4.0 SAMPLE COLLECTION**

This section describes procedures for setting the sampling pump and collecting ground water samples. Field data for these items will be recorded on the SIF for each sampling point.

### **4.1 Pump Setting**

No adjustments to the pump setting will be made in the residential wells to facilitate the groundwater sampling.

### **4.2 Sample Filtration**

No filtration of water well samples will be completed for residential wells.

### **4.3 Filling Sample Containers**

Table 1 summarizes the sample container type, filling method, preservation method and holding time for each analytical parameter set. To clarify and supplement the summary in Table 1, the manner in which containers will be filled is described below in subsections of 4.3. Individually prepared bottles will not be opened until they are to be filled with water samples. Special care will be taken to ensure that the procedures listed below are followed:

1. The area surrounding the sample collection point will be kept as clean as practical to minimize the potential for contamination of samples.
2. Care will be exercised to minimize the potential for airborne contamination of sample water during collection. If vehicles or generators are left running during sample collection, containers will be filled upwind from engine exhaust sources. If conditions are dusty, efforts will be made to shield the sample collection area from windborne contamination.
3. A clean and dry sheet of relatively inert plastic shall be placed on the ground surface in the wellhead area.
4. If materials used in the sampling process must be put down, they will be placed on a clean portion of the plastic sheet instead of the ground surface.
5. A clean pair of gloves will be put on at the onset of sampling activities at each new sampling point.

Sampling personnel will keep their hands as clean as practical and replace gloves if they become soiled while performing sampling activities.

6. Sampling personnel will not touch the inside of sampling containers, inside of bottle caps or rim of sample containers. If contact occurs, sample containers will be replaced.

At the well, bottles will be labeled and chain-of-custody sections will be filled out by the field personnel according to procedures described below in Section 5: "Documentation of Sampling Event". To prevent a mix up with sample bottle identification, no sampling-point specific information such as "well name" will be filled out in advance. Chain of custody information will be completed before leaving the sampling point. Laboratory provided and prepared bottles will be used to assure quality control.

The order of filling bottles with water to be analyzed will be as follows:

1. Major and minor ions
2. Nitrates, Chlorides
3. Trace metals
4. "Miscellaneous" parameters (Total Suspended Solids)
5. Non-volatile organics (Acrylamide)

Methods for filling sample containers for individual analyses are described.

The sample water discharge point at the end of the tube will be held as close as possible to the sample container without allowing the sample tubing to contact the container. At a minimum, sampling personnel will use their body to shield the sampling container from wind and airborne dust while filling. When strong winds, heavy rain, or dusty conditions are present, additional measures will be implemented to guard against background interference.

### **Nitrate**

Sample containers for nitrate analysis will be prepared in advance by the laboratories with sufficient  $H_2SO_4$  as a preservative such that the sample pH will be lowered to less than or equal to  $pH = 2$ . The containers will be filled approximately 95% full with unfiltered water. Containers will not be rinsed or overfilled at any time in the field.

### **Trace Metals**

Sample containers for general trace metals analysis will be prepared in advance by the laboratories with  $HNO_3$  as a preservative. This will insure that samples will be acidified as soon as they are collected. Containers will be filled approximately 95% full. Containers will not be rinsed or overfilled at any time in the field.

***Residential Wells*** Unfiltered (whole water) samples will be collected for the residential wells. The whole water samples will be analyzed for the residential wells.

### ***General***

All filtered sample water will be filtered through a 0.45 micron pore size filter unit before filling the laboratory prepared bottle. New filters will be used for each sample.

If sample water is too turbid to field filter and a pre-approved protocol exception has been developed, the sample will be collected in a new un-acidified container, put on ice, and

immediately delivered to the laboratory for filtration and acidification. Un-acidified metals sample bottles will be filled completely.

Whether filtered or not, samples for metals analysis will be collected in a manner that minimizes turbulence and aeration and then acidified immediately as described above. Plastic containers will be used for sample collection. The acid will be produced/controlled within the applicable QA/QC program to ensure that it is pure enough (e.g., Ultrex or pure acid diluted with triple distilled water) with regards to metals to avoid a false positive analytical result.

### **Non-Volatile Organics**

As defined here, "non-volatile organics" (meaning organic compounds that are not highly volatile) include acrylamide. Sample containers used for non-volatile organics analysis will not be rinsed in the field or allowed to overflow excessively during sample collection. Containers will be filled completely.

### **4.4 Field Blanks, Replicate And Split Samples**

Replicate samples will be collected to evaluate variability in analytical methods. QA/QC samples will be collected at sampling points suspected to have relatively higher levels of contamination to provide meaningful information duplicate sample evaluation. All QA/QC samples will be collected in the same type of container as the corresponding primary samples. All QA/QC samples will be assigned identification aliases on the sample bottle label and on the chain of custody sheet to avoid alerting laboratories that the sample is a blank or replicate sample. The true identity of the QA/QC samples will be recorded in the Field Log.

The collection schedule for QA/QC samples will be as follows:

At least one duplicate sample for every sample round collected (TSS, Nitrates, or Trace Metal)

### **Field Replicate (Duplicate) Samples**

Field replicate samples of actual ground water will be collected and analyzed for the same parameters as the primary samples are analyzed for. Replicate samples will be collected for 10% of the primary samples collected. Replicate samples will be collected by sequentially filling all containers as close together in time as practical with a sampling stream that is as steady and continuous as practical. The sequence number (first, second, etc.) and time filled will be listed in the field notebook. The time that each individual container was filled will be listed on the container and on the Sample Identification - field chain of Custody Record in the same manner as primary samples. One field replicate sample set will be collected for every ten primary sampling sets.

Baseline Samples that identify the presence of Acrylamide will be resampled.

## **5.0 DOCUMENTATION OF SAMPLING EVENT**

This sampling protocol includes the use of a Chain of Custody Form similar to that identified by the WDNR as Form 4100-145. Specific information that will be recorded in the Field Log for each sampling event includes:

1. Date
2. Time of Sample
3. Prevailing Weather Conditions (temperature, wind speed and direction, cloud conditions, precipitation)

4. Sample Technician
5. Sample Location – resident name and residence address, water spigot location, spigot and well conditions
6. Estimated Pump Rate
7. Volume of Well Water Purged

## 5.1 Sample Identification

The Chain of Custody form will be completed as described above in Section 5.0, "Documentation of Sampling Event". All primary and QA/QC samples collected at a given sampling point over a discrete interval of time will be assigned the same sample event ID #. This number is used to link that set of sample containers together and associate them with the information gathered to that sample point.

Each sample container will be labeled with the following information using a waterproof marker on firmly affixed, water-resistant labels:

1. Unique container ID #
2. Sample collection Date
3. Sample collection Time
4. Initials of person collecting sample
5. Analyses required on pre-printed label
6. Preservation method specified on pre-printed label when preserved at lab
7. Sampling organization name on a pre-printed label

Container information will be entered at the sampling point at the time of sample collection with the following exceptions. For containers receiving preservatives in advance, "analyses required" and "preservation method" will be entered onto labels by laboratory staff. For containers receiving preservatives in the field, "preservation method" will be entered at the time individual containers are filled.

## 5.2 Chain Of Custody

A chain-of-custody record will be initiated in the field at the time of sampling; a copy will accompany each set of samples (cooler) shipped to any laboratory.

Each time responsibility for custody of the samples changes, the new and previous custodians will sign the record and denote the date and time. A copy of the signed record will be made by the receiving laboratory. The final signed chain-of-custody will be submitted with analytical results in the Sampling and Analysis Report.

### Field Chain of Custody Documentation

All signatures related to sample custody will be made in ink on the chain-of-custody in a timely fashion. One or more signatures will be entered to identify the person or persons who are collecting the samples. Each time the custody of a sample or group of samples is transferred, a signature, date and time will be entered to document the transfer. The signatures, date, and time will be entered at the time of transfer. A sample will be considered to be in custody if it is in any one of the following states:

1. In actual physical possession
2. In view, after being in physical possession
3. In physical possession and locked up so that no one can tamper with it

4. In a secured area, restricted to authorized personnel

A secured area such as a locked storage shed or locked vehicle specified in the "comments" column, may be used for temporary storage. When using such an area, the time, date, and location of the secured area will be recorded in the "relinquished by" space. The time at which an individual regains custody will then be recorded in the "received by" space.

### **Chain of Custody during Shipping and Transfer of Samples**

When samples are shipped, the person sealing the shipping container will enter the time, date and their signature on the chain-of-custody. The laboratory part of the chain-of-custody will be enclosed in the container; a copy will be retained for the Sampling Consultant's file.

**Custody seals are not required for this project.**

### **5.3 Field Sampling Log**

A daily field log of sampling activities will be kept by the leader of the field sampling crew. This record or log will supplement information entered on the SIF. At a minimum, the log will contain a record of the following items:

1. List of field personnel present
2. Field conditions as described below in Section 5.5, "Field Conditions"
3. A summary of how samples were transferred/transported to laboratories
4. Description of exceptions to this protocol including specification of which samples may have been impacted by exception(s) (see below)
5. For each well sampled:
6. The unique Chain of Custody number used to identify samples
7. Well name and Wisconsin unique well number
  - a. Date and time that sampling began and ended
  - b. List of primary and QA/QC samples sent to each laboratory
  - c. Any alias cross-reference list for QA/QC samples

### **5.4 Exceptions To Sampling Protocol**

This protocol defines the procedures to be followed during this sampling event. Exceptions to this protocol will be noted on the Chain of Custody and detailed in the Field Log (see above). The section titled "Exceptions to Protocol" in the Sampling and Analysis Report will include the following details for each exception:

1. The reason for the exception
2. The identification of all samples and individual parameters that may have been impacted either in terms of the quantitative or legal integrity of their reported values
3. The significance of the potential impacts to the integrity of each parameter for each sample

If there has been any potentially significant impact on sample integrity, then the potential impact for each parameter for each sample affected will be footnoted whenever the results are reported or referred to in the Sampling and Analysis Report.

### **5.5 Field Conditions**

Field conditions during the sampling event will be recorded in the Field Log. The Sampling and Analysis

Report will include a statement regarding the likelihood that any unusual field conditions had a significant impact on the integrity of results. Field conditions reported will include but not be limited to the following:

1. Air temperature
2. Wind speed
3. Precipitation/moisture
4. Ambient odors
5. Airborne dust

## **6.0 SAMPLE PRESERVATION, HANDLING AND TRANSPORT**

This section describes procedures that will be followed between the time samples are collected and the time they are either shipped or delivered to an analytical laboratory.

### **6.1 Sample Preservation**

Samples will be preserved as shown in Table 6-1. All chemical preservatives, added to containers in the laboratory or field will be produced and controlled within the laboratory's QA/QC program. Field supplies of preservatives and sample containers with pre-dosed preservatives will be discarded and replaced with fresh preservatives no later than 14 days after receipt from the laboratory.

All samples will be thermally preserved in the field immediately after sample collection by placing the samples in an insulated ice chest containing uncontaminated ice. Particular care will be taken to assure that paper work and sample labels are not damaged by water by placing the records inside a Zip Lock bag. The ice chest temperature will be checked by measuring the temperature of the water within the temperature blank container and recorded just before transporting samples and upon receipt at the laboratory, to verify whether or not samples are kept refrigerated at approximately 4 degrees C.

### **6.2 Sample Handling and Transport**

All ice chests shipped will be accompanied by a Chain of Custody form and contain a complete address and return address both inside and out. The samples will be kept at approximately 4°C during transport to laboratories. Before transporting samples, field personnel will perform the following tasks:

1. Verify that laboratory personnel will be present to receive samples when they arrive.
2. Verify that laboratory personnel understand chain of custody and sample storage/preservation requirements.
3. Check labeling and documentation to ensure sample identity will be clear to laboratory personnel.
4. Hand deliver or ship samples in a manner that ensures samples will remain cool (about 4°C) until received by laboratory personnel.
5. Maintain the chain-of-custody according to procedures described above.



**Table 6-1: Sample Containers, Filling Method, Preservation and Holding Times**

Table 1				
PARAMETER	BOTTLE VOLUME/TYPE	FILL METHOD	PRESERVATION	HOLD TIME
Total Suspended Solids	1 liter polyethylene	Leave head space	Cool	7 days
Coliform Bacteria	250 ml Polyethylene	Leave Head Space	Lab Sterile, Cool	24 hours
Nitrate –Nitrogen	250 ml Polyethylene	Leave Head Space	H <sub>2</sub> SO <sub>4</sub> < 2, Lab, Cool	28 days
Chlorides	125 ml Polyethylene	Leave Head Space	H <sub>2</sub> SO <sub>4</sub> < 2, Lab, Cool	28 days
Lead and Arsenic	500 ml Polyethylene	Leave Head Space	HNO <sub>3</sub> < 2, Lab, Cool	6 months
Acrylamide	125 ml Amber Glass	No Head Space	Cool	7 days

**(1) PARAMETER NAMES/GROUPS**

Some of these parameter names {e.g., "trace metals"} actually represent a set of several or many individual analytes. Specific analytes for each parameter/bottle type are listed in the Scope of Work.

**(2) FILL METHOD**

No head space - fill container completely; container will not be rinsed; overfilling will be minimized.  
 Leave head space - fill container about 90 to 95% full - do not allow preservative (if present) to be diluted by overfilling container. Filter [0.45 micron] - filter in-line with positive pressure through a filter with 0.45 micron pore size.

**(3) PRESERVATION**

Cool - place sample container inside sealed Zip-Lock bag; place in cooler with sufficient ice to quickly bring temperature down to 4 °C and hold at approximately 4 °C until received by laboratory personnel.  
 H<sub>2</sub>SO<sub>4</sub>/pH<2 - add a predetermined amount of high-purity H<sub>2</sub>SO<sub>4</sub>, to sample to bring the sample pH down to 2 or less.  
 HNO<sub>3</sub>/pH<2 - add a predetermined amount of high-purity HNO<sub>3</sub>, to sample to bring the sample pH down to 2 or less.  
 Lab - preservative added to container in laboratory before going into the field.